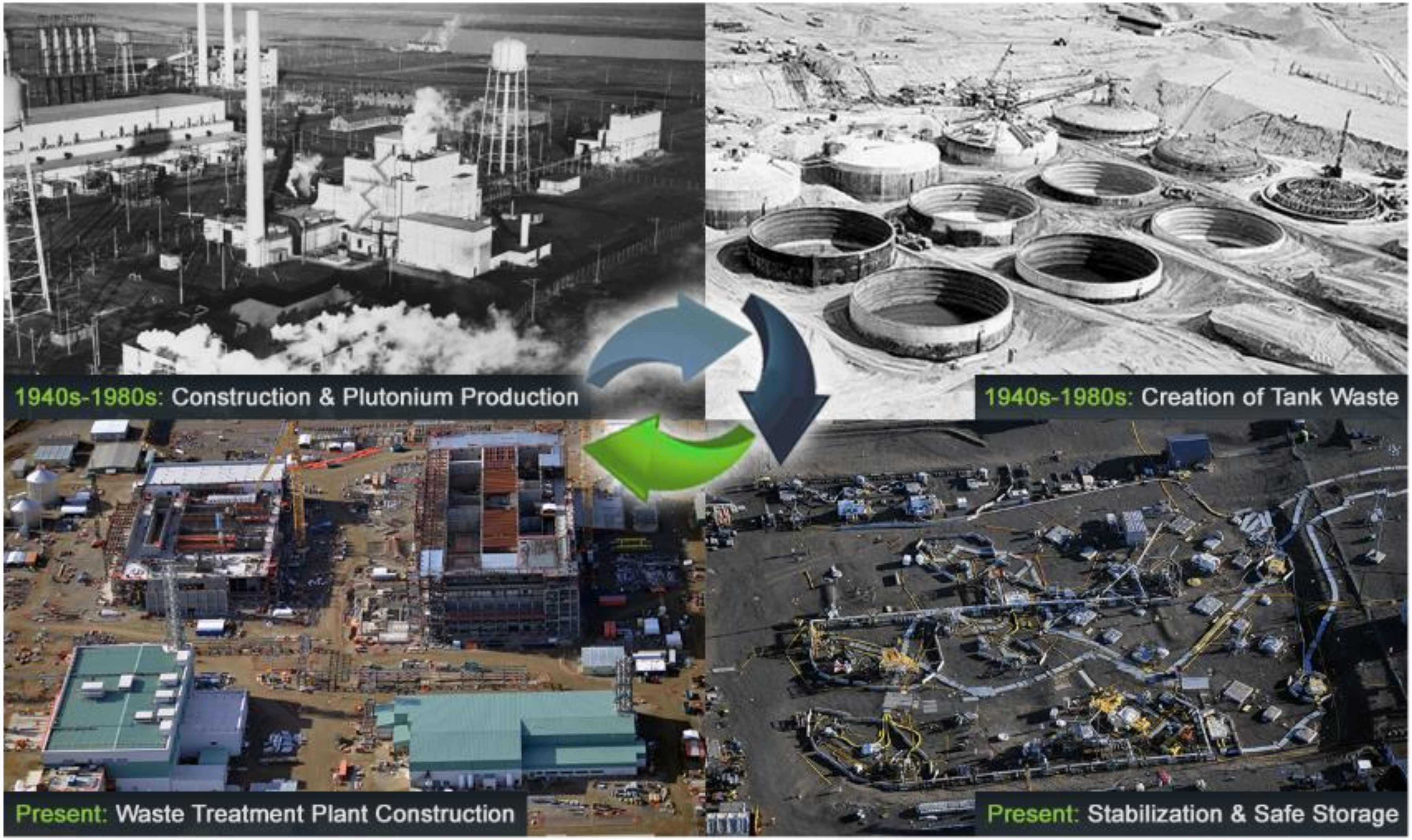
OFFICE OF
RIVER PROTECTION
United States Department of Energy

Enhanced Waste Glass Effort

Presented by: **Albert Kruger, U.S. Department of Energy, Office of River Protection**

March 2019

Hanford Historical Overview



Tank Farm Mission

Safely maintain 56 million gallons of radioactive and chemical waste

- 1943-1964: 149 single-shell tanks (SST)
- 1968-1986: 28 double-shell tanks (DST)

Generation of Hanford Tank Wastes

9 Reactors; 4 Fuel Reprocessing Flowsheets; 100,000 MT Fuel Processed

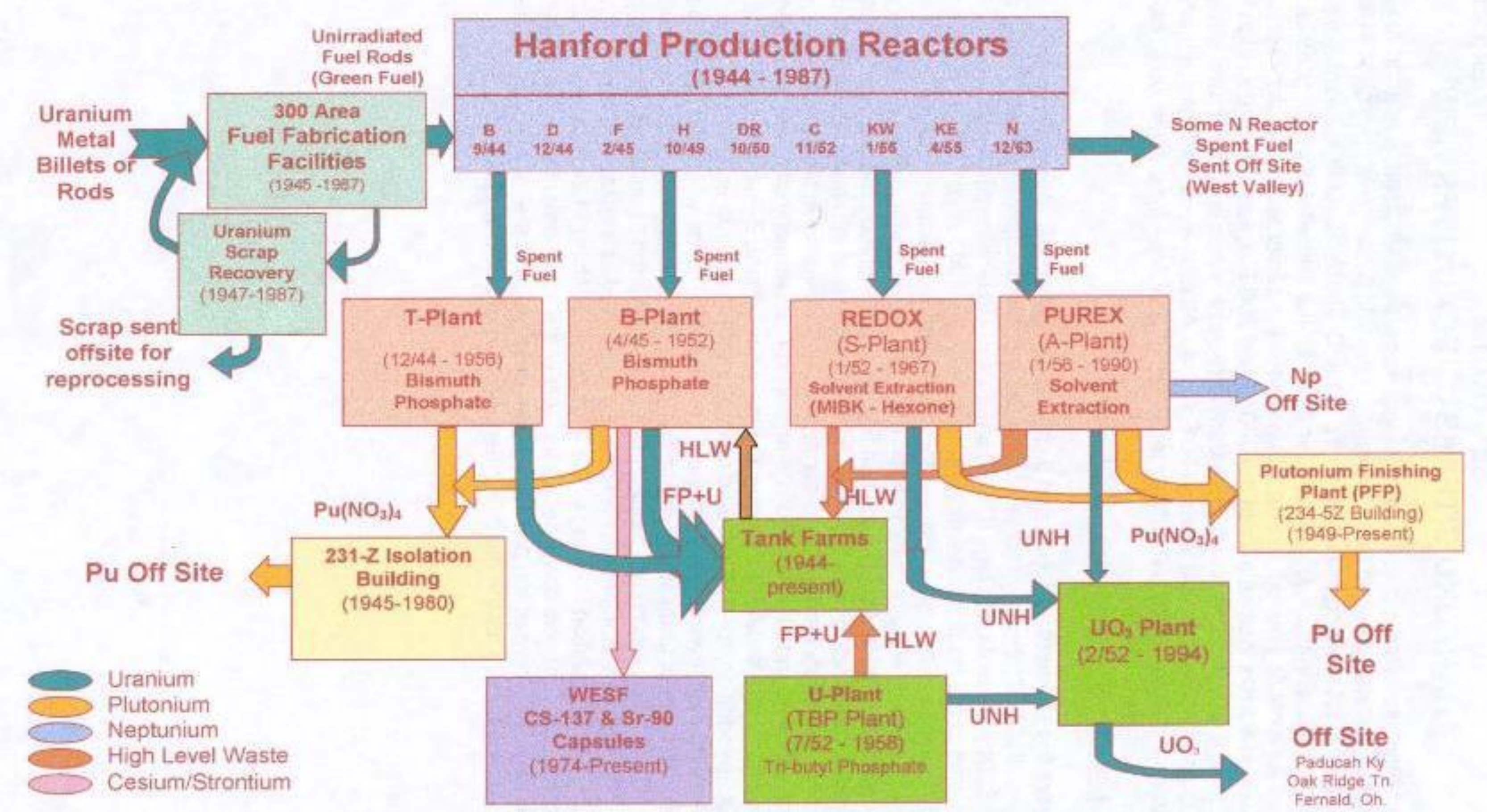
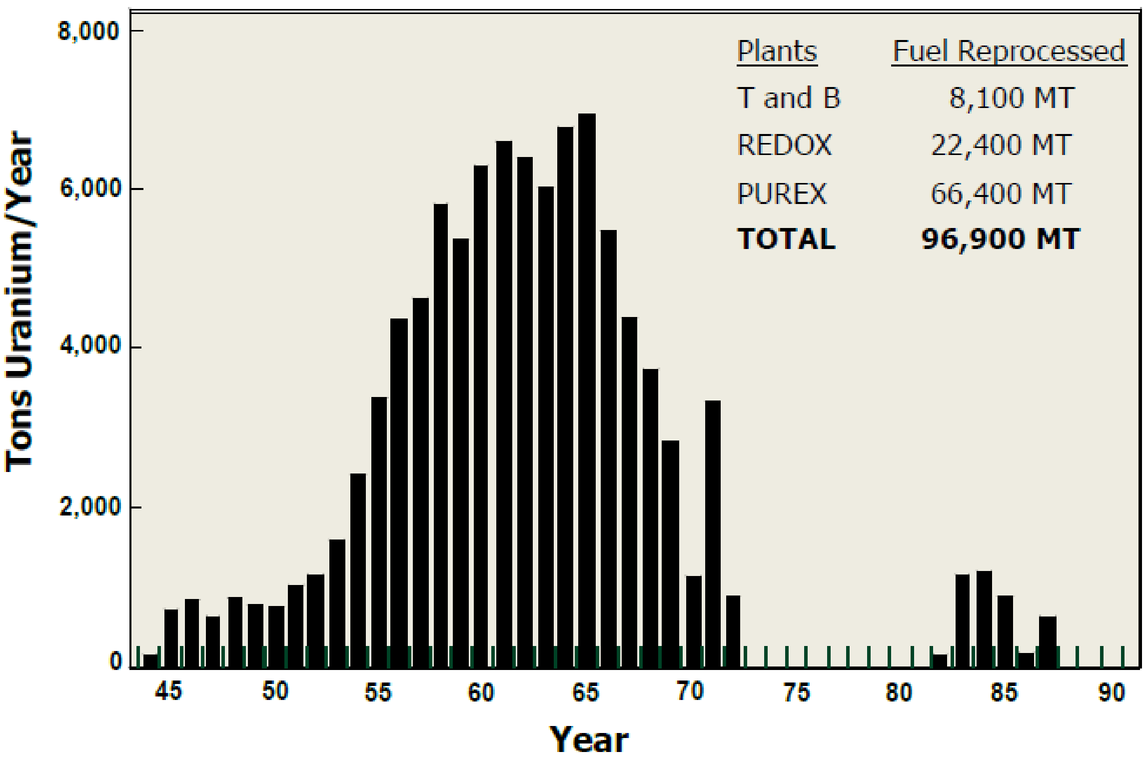
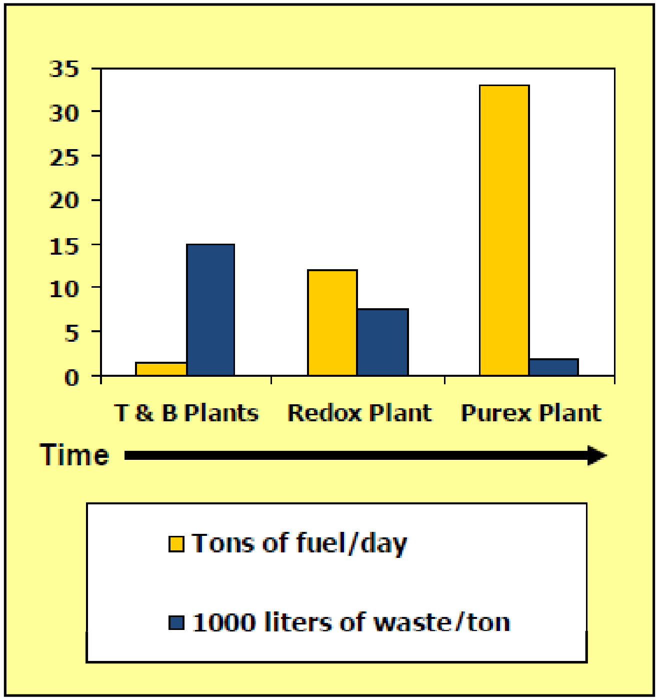


Figure 2-2 Hanford Major Process Flows and Facility Interfaces

Generation of Hanford Tank Wastes





What's in the Tanks

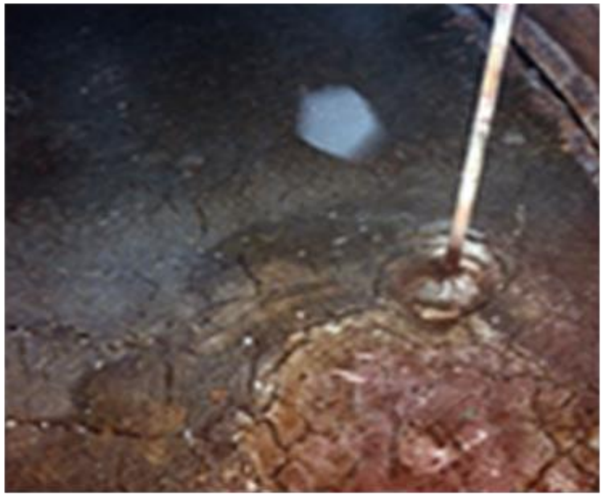
Saltcake
23M gallons

Mostly water-soluble salts; small amount of interstitial liquid

Supernate
21M gallons

Any non-interstitial liquid in the tanks – similar to saltcake in composition

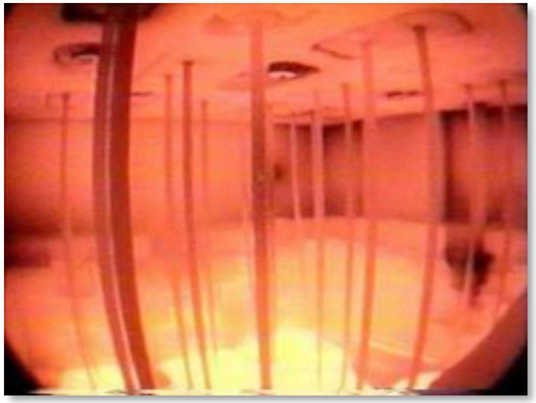
Sludge
12M gallons



Water-insoluble metal oxides, significant amount of interstitial liquid – texture similar to peanut butter

Waste Treatment and Immobilization Plant

WTP Mission: Immobilize Waste in Glass



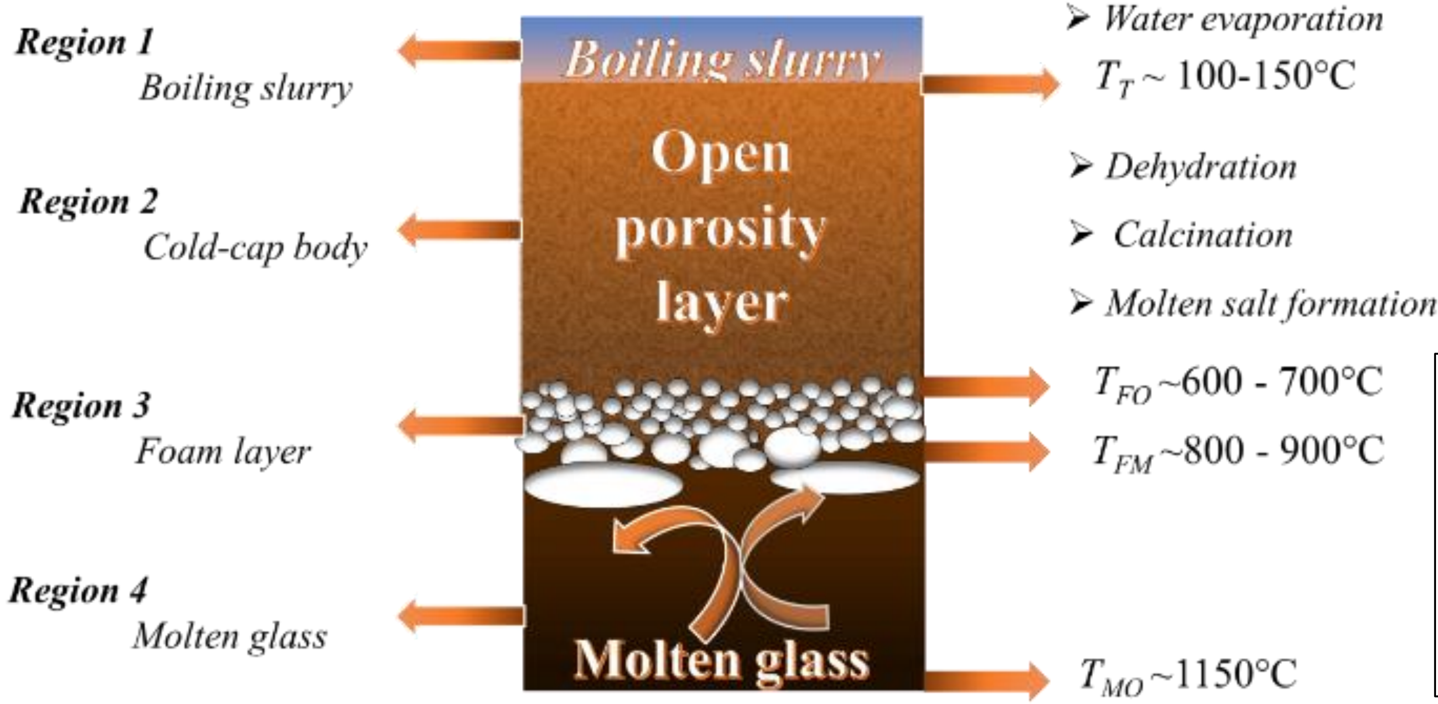
Molten glass and waste in a melter

Simulated vitrified waste

High-level waste (HLW) and low-activity waste (LAW) containers

Simulated vitrified waste in a container

Enhanced Heat Flux By Bubbling



TT is the cold-cap top temperature, TFO is the foam onset temperature, TFM is the foam maximum temperature (preceding the foam collapse), and TMO is the melter operating temperature.

- Primary foam related to CO2 gas goes down, grows, coalesces, and creates a cavity in the foam layer
- Secondary foam related to O2 gas goes up and accumulates under the cavity (or some foam maybe burst into the cavity) in the bottom of the cold cap
- Gases in the cavity tends to move to the side of the cold cap and burst to atmosphere

Selected Pellet Photos

AN-102




625°C 675°C 725°C 775°C

AZ-102





AN-102

820°C 860°C


AZ-102

What's New?

- Recent changes to the glass formulation?
  - Projections Volumes of Glass for the Mission
- What are the key physical properties that should be used to compare glass to other stabilization types?

C3T, 2002, "Record of Meeting for Mission Acceleration Initiative – Supplemental Technologies C3T Decision Criteria Workshop" (July 31), CH2M HILL Hanford Group, Inc., Richland, WA

WTP Glasses

All WTP glasses considered to date are alkali borosilicates

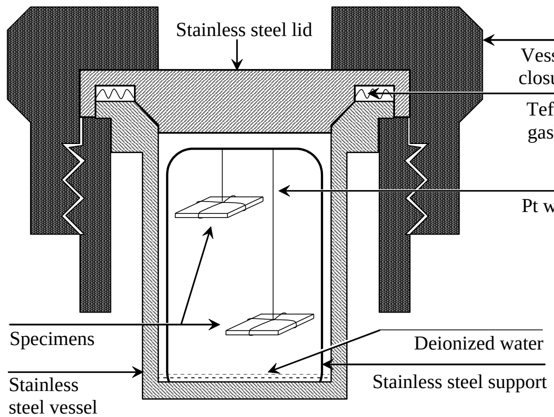
- Crystalline phase identification
- Radiological composition documentation
- Radionuclide concentration limitations
- Surface dose rate limitations
- Surface contaminations limitations
- External temperature
- Free liquids
- Pyrophoricity or explosivity
- Explosive or toxic gases
- Waste form testing in leachablity, product consistent testing, and vapor hydration testing
- Thermal, radiation, biogradation, and immersion stability
- Dangerous waste limits
- Container material degradation

Letter S. Dahl-Crumpler to R. J. Schepens, "Supplemental Treatment for Tank Waste," April 25, 2003.
Letter R.J. Schepens to M. A Wilson, "Response to Concerns Regarding U.S. Department of Energy (DOE) evaluation and use of Supplemental Technologies for Treatment of Tank Wastes," 03-ED-091, June 12, 2003.

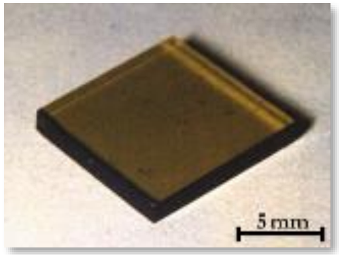
Progress in Glass Chemistry and Science

Durability Tests to Qualify Wastes

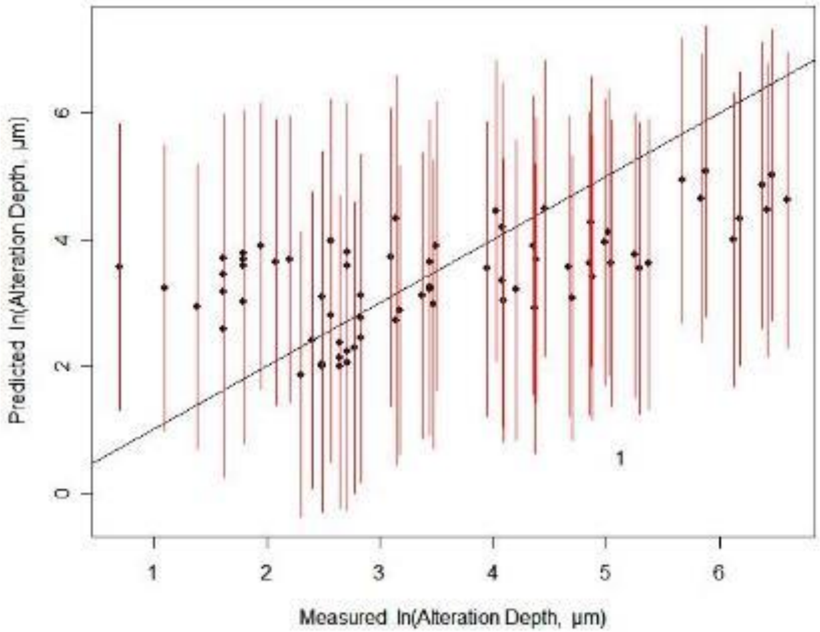
*2.2.2.17.3 "The glass corrosion rate shall be measured using at least a seven (7)-day vapor hydration test run at **200°C**". "The measured glass alteration rate shall be less than 50 grams/(m^2 day)".*



0 days



15 days

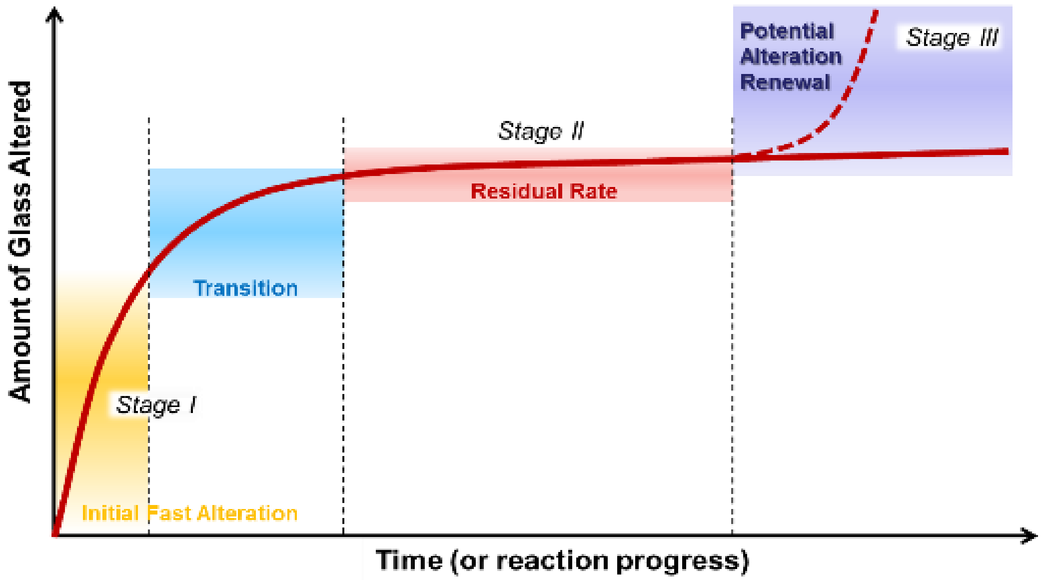


The Vapor Hydration Test (VHT)

- ✘ High variability between labs
- ✘ High variability between operators
- ✘ Inconsistent with assessment of glass durability under the anticipated disposal conditions
- ✘ Large uncertainties in dissolution rate

Glass Corrosion: Accelerated Aging Tests

- Stage I: Hydrolysis of the silicate network, followed by rapid dissolution and ion exchange between the glass and altering medium
- Stage II: Dissolution rate decreases and levels out as gel-like alteration layer is stabilized, pseudo equilibrium between formation and dissolution of alteration layer
- Stage III: Glass alteration rates increase concomitant with the precipitation and growth of crystalline secondary phases (zeolites, magnesium silicates, iron silicates, etc.)



Stage I and II testable by short-term accelerated aging experiments, but Stage III less well understood

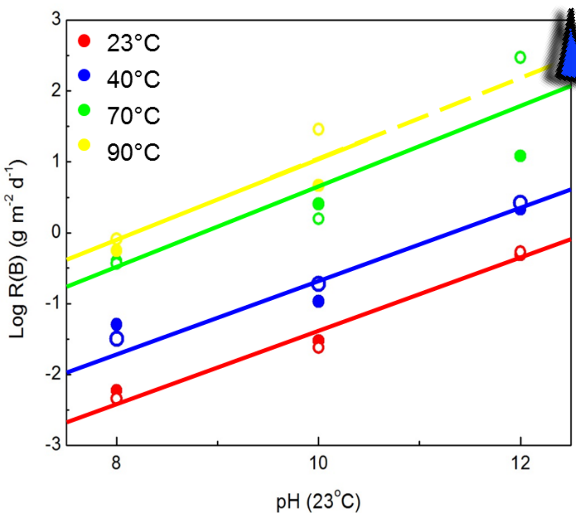
Performance Assessment?

Transition State Theory

$$R_i = k_0 v_i e^{-E_a/RT} a_{H^+}^n \left[1 - \left(\frac{Q}{K}\right)^{\sigma}\right]$$

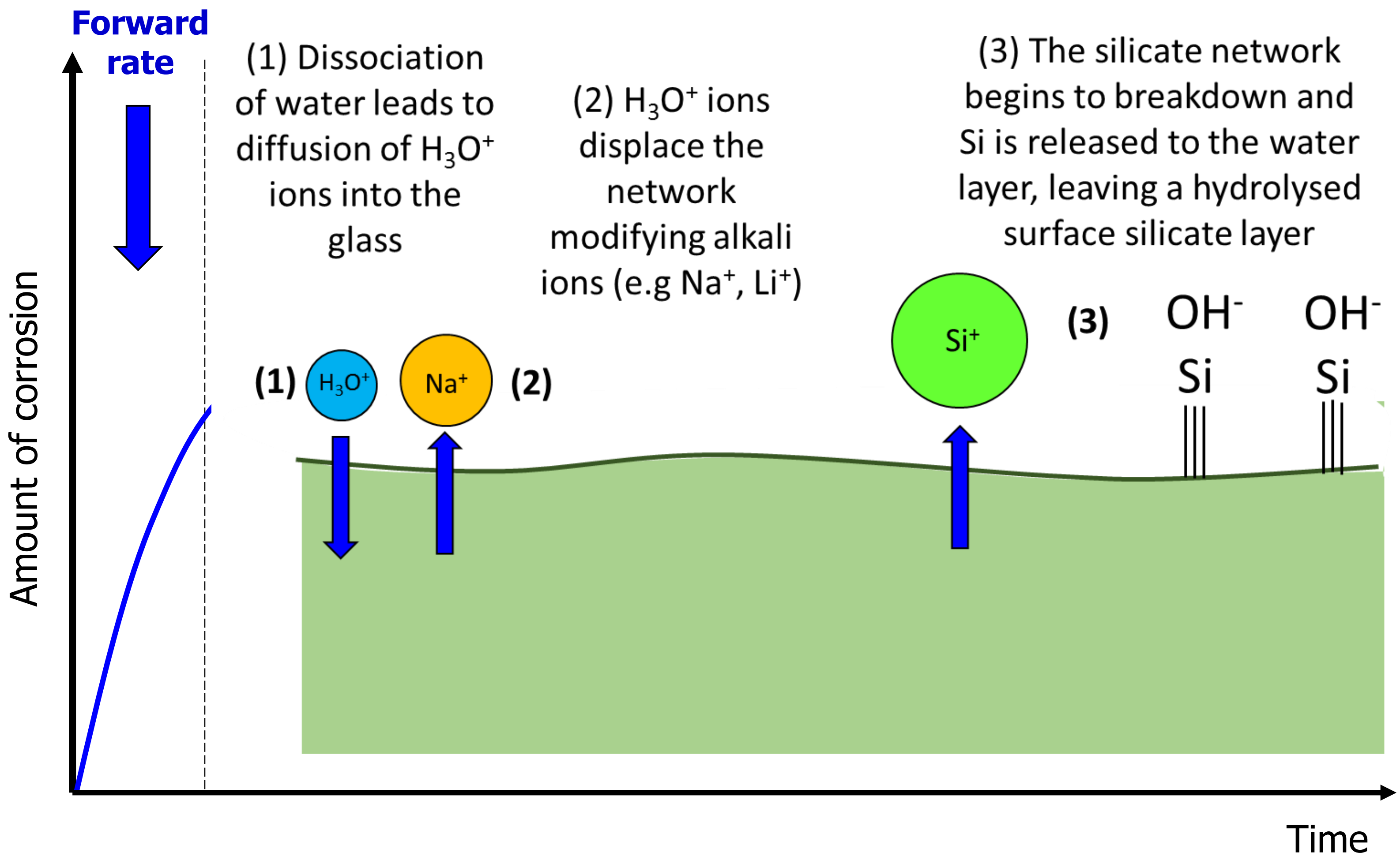
Rate Constant (k_0); Activation Energy (E_a); "Affinity Term" $\left[1 - \left(\frac{Q}{K}\right)^{\sigma}\right]$; Dissolution Rate ($R_i$); Stoichiometric Function (v_i); Proton Activity ($a_{H^+}^n$)

If we are in the "forward rate" the affinity term becomes zero and we can determine the dependence of dissolution rate on temperature and pH for performance assessment

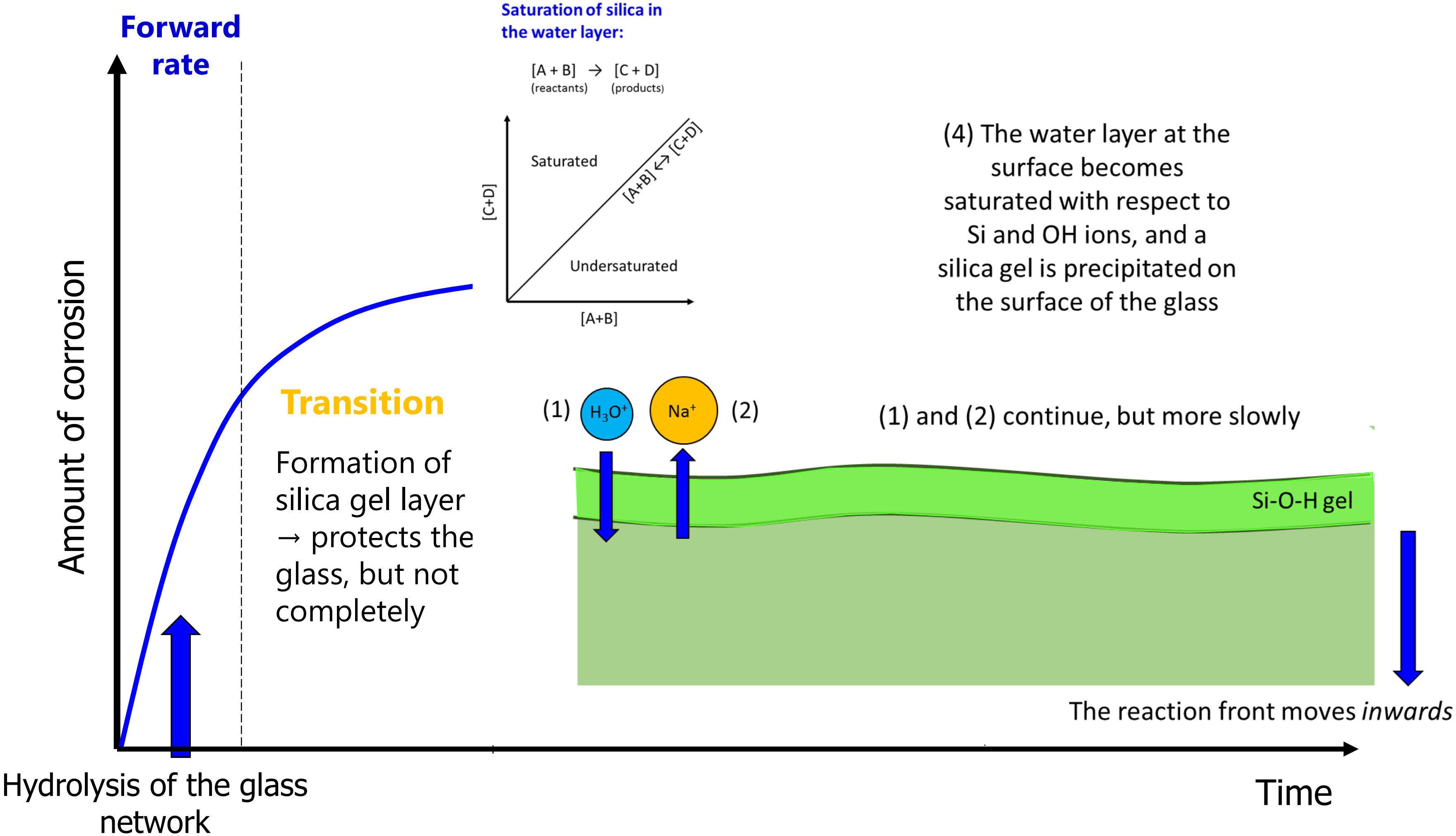


- Results typically obtained by Single Pass Flow Through (SPFT) experiments
- Very convoluted measurements
- Expensive to perform!

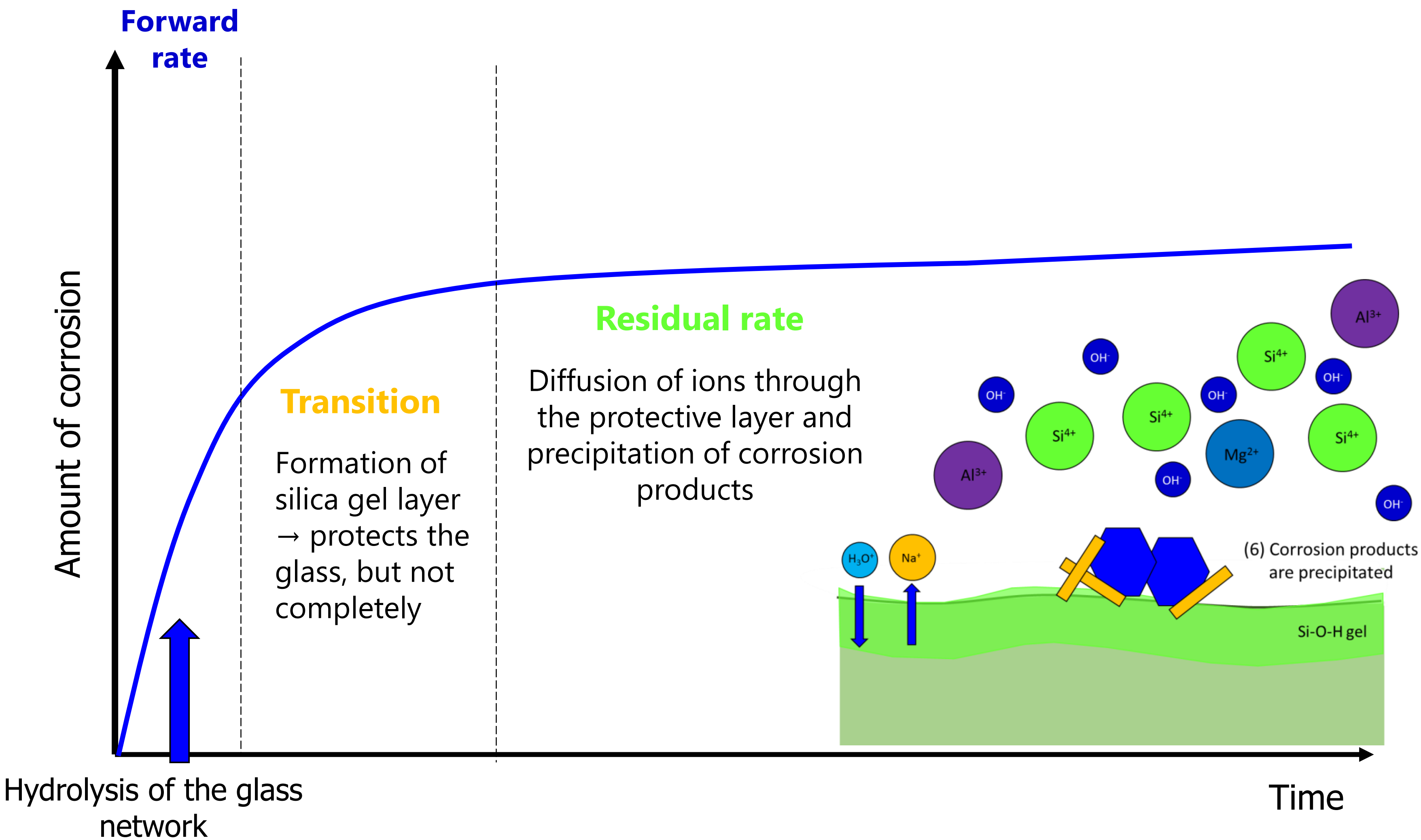
Are we in the "Forward rate"?



Or the "Transition" or "Residual" rates?



Or the "Transition" or "Residual" rates?



Broborg Project Objectives

- Determine the long-term durability of Broborg hillfort glass to support putting Hanford low-activity waste (LAW) glass in the Integrated Disposal Facility (IDF).
- Provide further insight into the anthropological and archeological interpretation of the Broborg Hillfort Site, Sweden

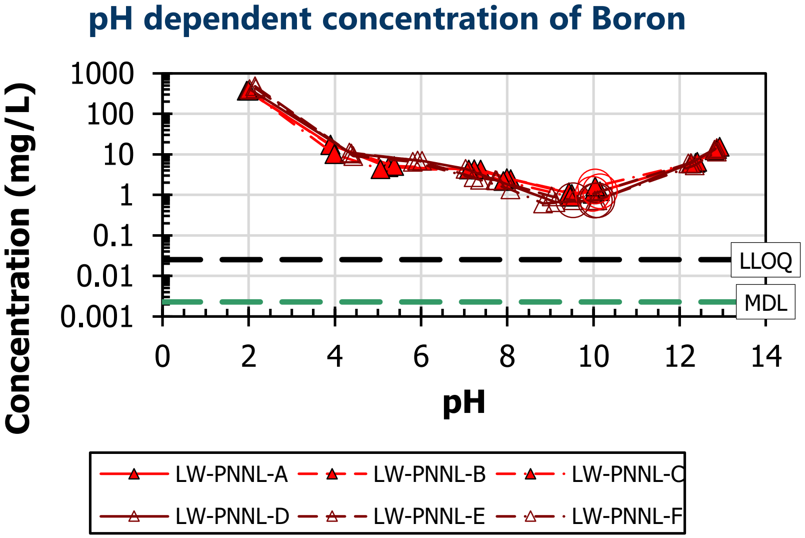
Glass analogues can be used to assess performance LAW glass for storage of radioactive waste for 10,000+ years

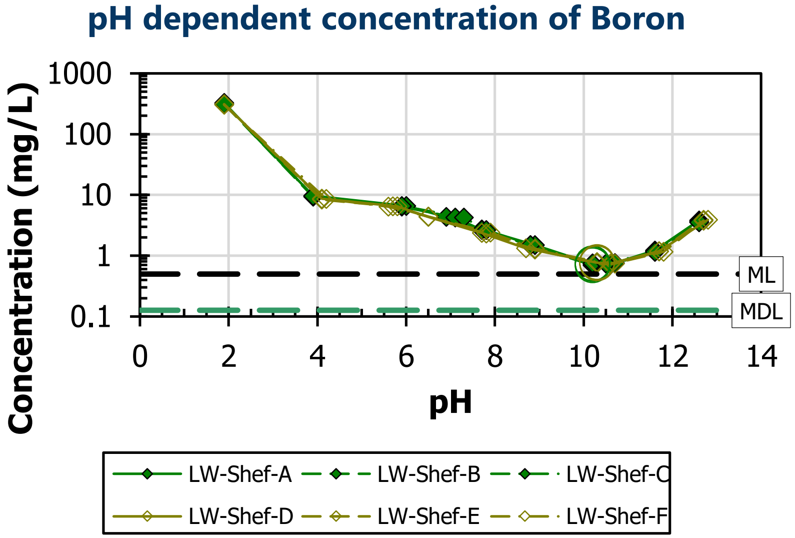
Ages of ancient glasses vs. nuclear waste glasses (not to scale)

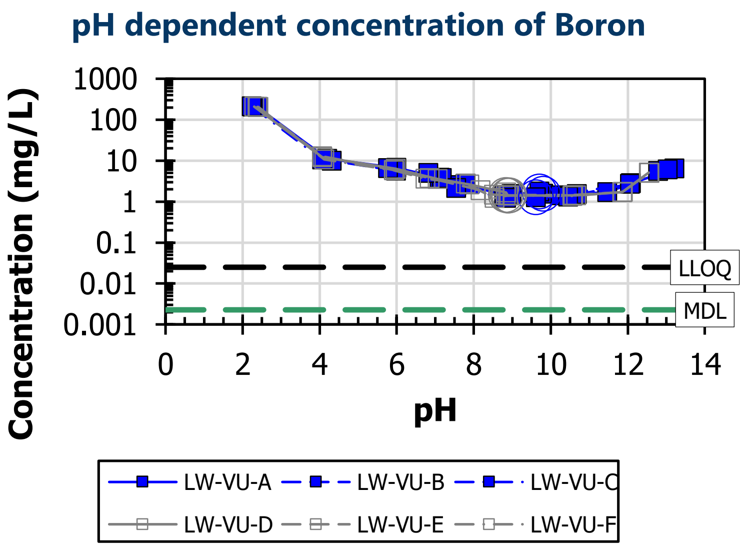
Summary

- Broborg glasses fulfill several important prerequisites for good analogues for nuclear waste glass:
    - Similar chemical composition
    - Similar mechanisms of corrosion
    - Alteration in similar, known environmental conditions

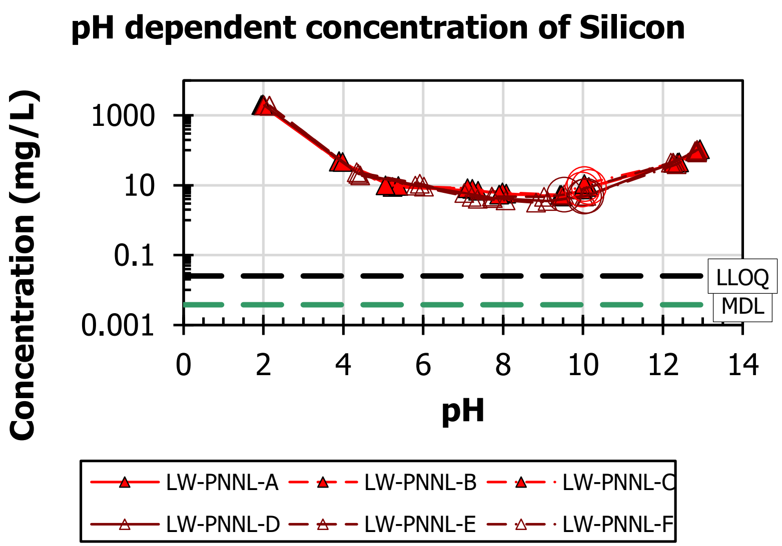
1313 Interlab Validation Data

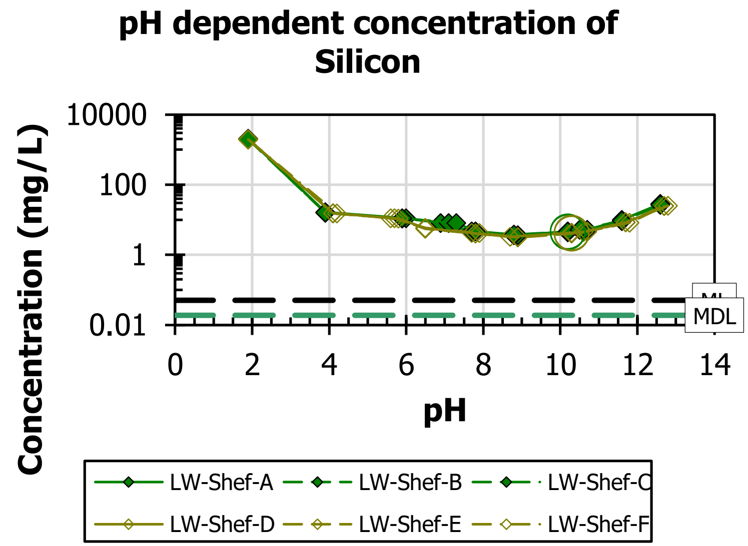


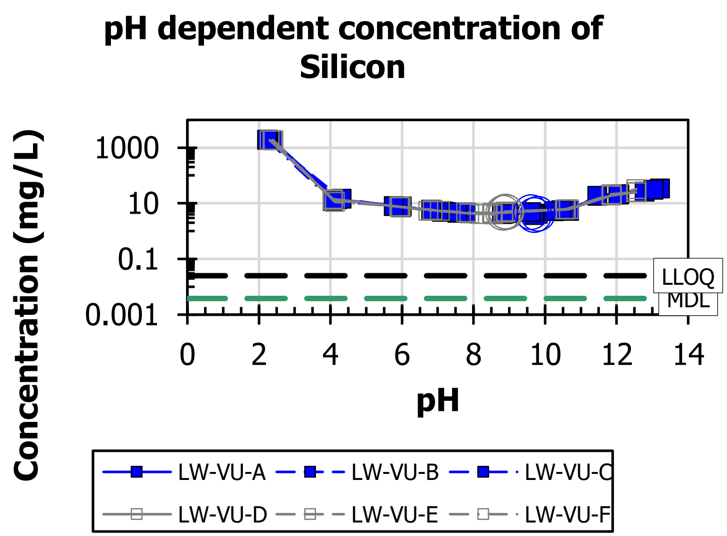




1313 Interlab Validation Data







Combined Project Objectives

The GLAD Project

Aim: To design a new test for LAW glass that is more representative of low temperature corrosion.

Develop a low temperature glass corrosion test

Confirm ease and reproducibility between three laboratories

Exchange the controversial VHT for the new test

The Hillfort Project

Aim: To validate the chosen low temperature test against natural analogues from 2,000-year-old Swedish Hillforts.

Take glass samples from Swedish Hillfort

Study corrosion and corrosion environment

Make glass of identical composition

Apply test to Hillfort glasses and validate

Projections Volumes of Glass for the Mission

Baseline Glass Model Impact on Treatment Mission

	BNI/WTP Baseline Models	2008 TUA* Baseline		
HLW Canisters	18,400	14,838		
LAW Containers	145,000	91,400		
Total Canisters & Containers	163,000	106,238		

* The "2008 models" were altered in anticipation of our work

24590-WTP-RPT-PE-13-003, Rev 0, 2013 Tank Utilization Assessment (TUA) Part 1: Potential Impact of Advanced Glass Models on the WTP, 3 December 2013

Enhanced Glass Model Impact on Treatment Mission

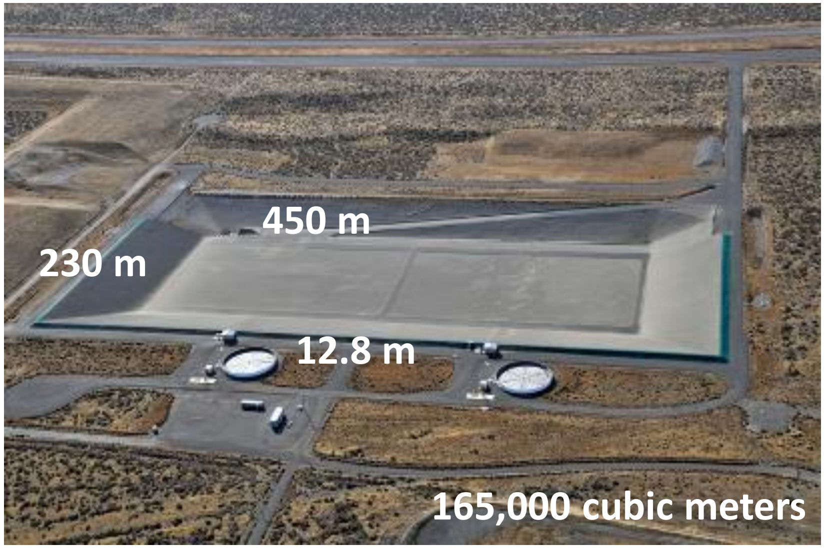
	BNI/WTP Baseline Models	2008 TUA* Baseline	2013 TUA Baseline	2013 TUA w/ caustic and oxidative leaching eliminated
HLW Canisters	18,400	14,838	8,223	13,534
LAW Containers	145,000	91,400	79,465	65,151
Total Canisters & Containers	163,000	106,238	87,688	78,685

* The "2008 models" were altered in anticipation of our work

24590-WTP-RPT-PE-13-003, Rev 0, 2013 Tank Utilization Assessment (TUA) Part 1: Potential Impact of Advanced Glass Models on the WTP, 3 December 2013

Low-Activity Waste Vitrification

Low-Activity Waste Glass

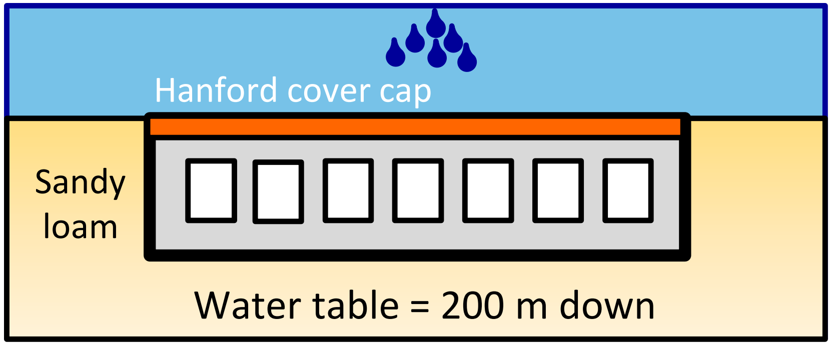


Integrated Disposal Facility

ILAW glass will immobilize:

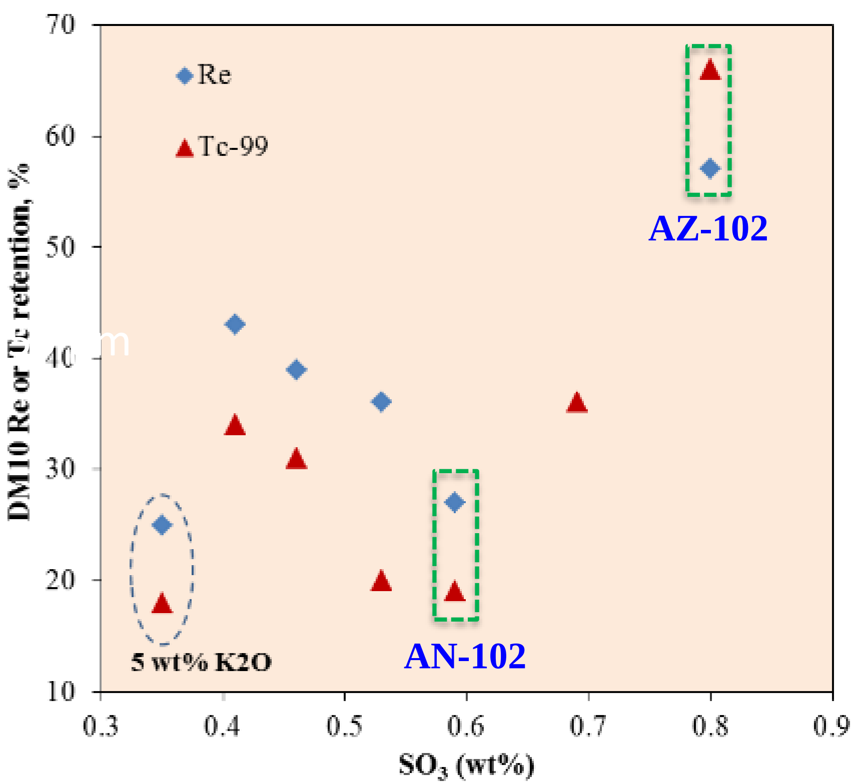
- Long-lived semi-volatile anions: $^{99}TcO_4$ (half-life 213,000 years) and ^{129}I (half-life 15.7 million years)
- Toxic metals: Cr, Ni, V
- High alkali content (Na and K)

- Average temperature: 60º F
- Rainfall: less than 7 inches per year



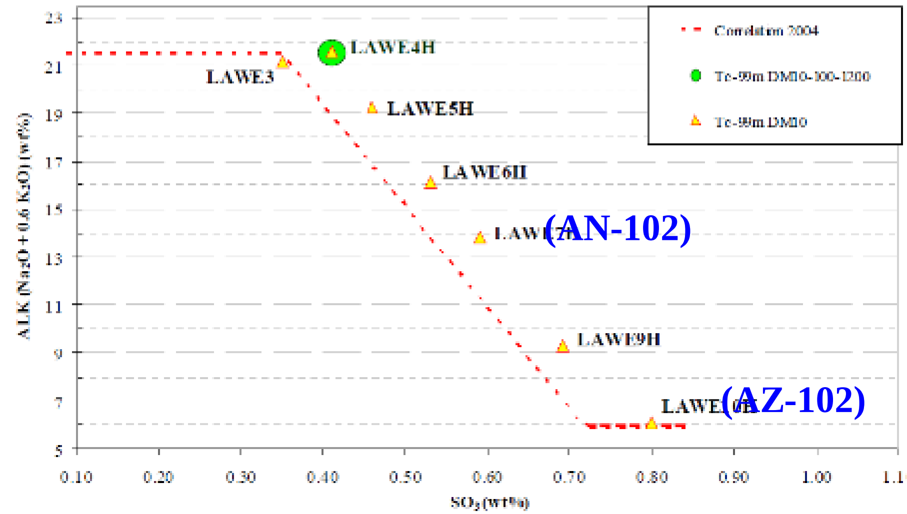
Selection of Feeds

Based on Re and ^{99m}Tc Retention Data from small-scale melter (DM10) Tests by Vitreous State Laboratory (VSL)



Data and plot from VSL-11R2260-1, Rev 0

"$Na_2O + K_2O$" wt% versus SO_3 wt% for 7 representative LAW feeds (WTP LAW glass formulation rules)

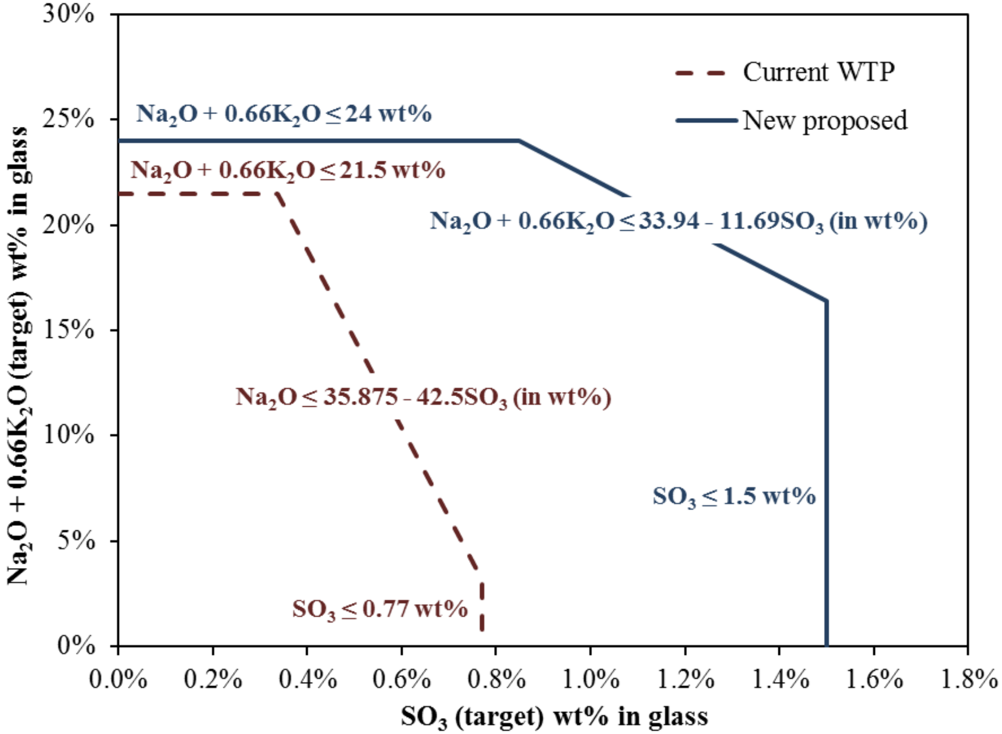


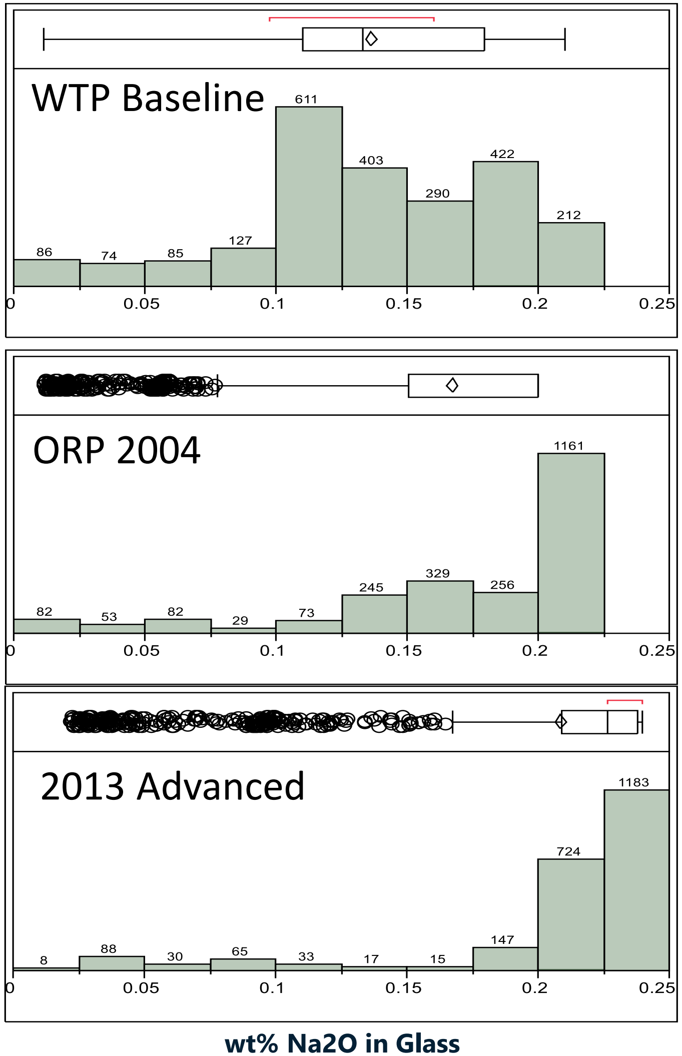
AN-102 and AZ-102 feeds with large difference in Re/Tc retention from DM10 tests were selected for initial set of crucible tests

- AN-102: medium sulfur, high nitrates
- AZ-102: high sulfur, low nitrates

Sulfur and Alkali Limits

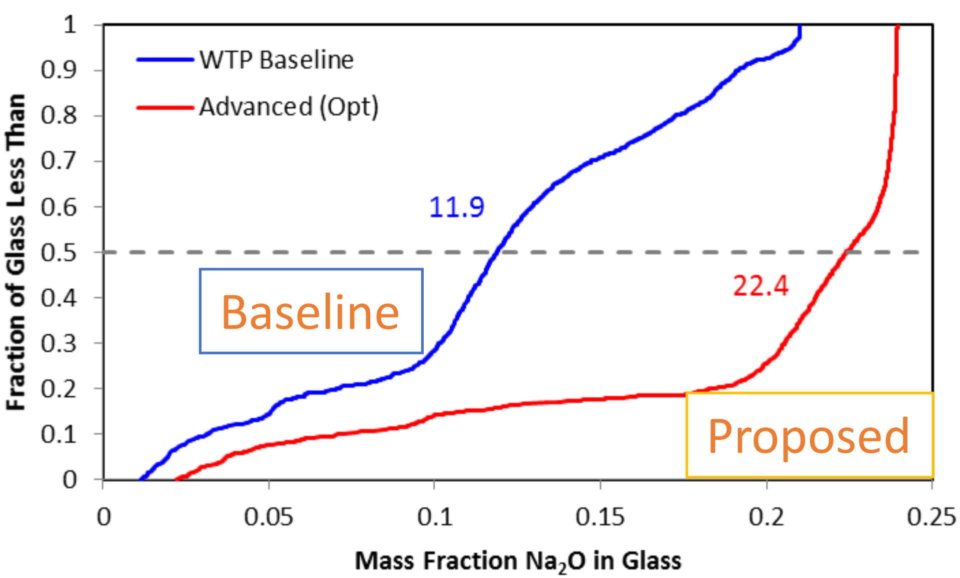
- The factors limiting LAW glasses are:
  - Chemical durability as measured by PCT and VHT for high Alk:SO_3 wastes
  - Salt accumulation for low Alk:SO_3 wastes and high halide wastes

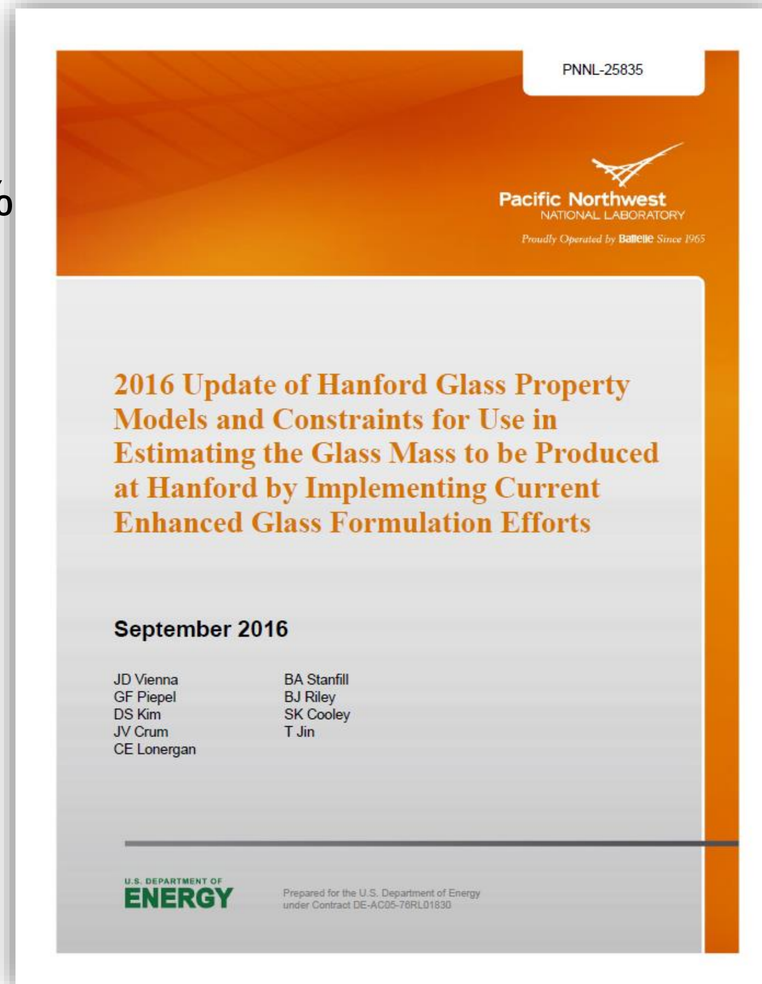




Models and Constraints

- A preliminary set of models and constraints developed and documented
- Waste loading changes range from slight (112% to over double (224%) (weighted average of roughly double)





PNNL-25835

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2016 Update of Hanford Glass Property Models and Constraints for Use in Estimating the Glass Mass to be Produced at Hanford by Implementing Current Enhanced Glass Formulation Efforts

September 2016

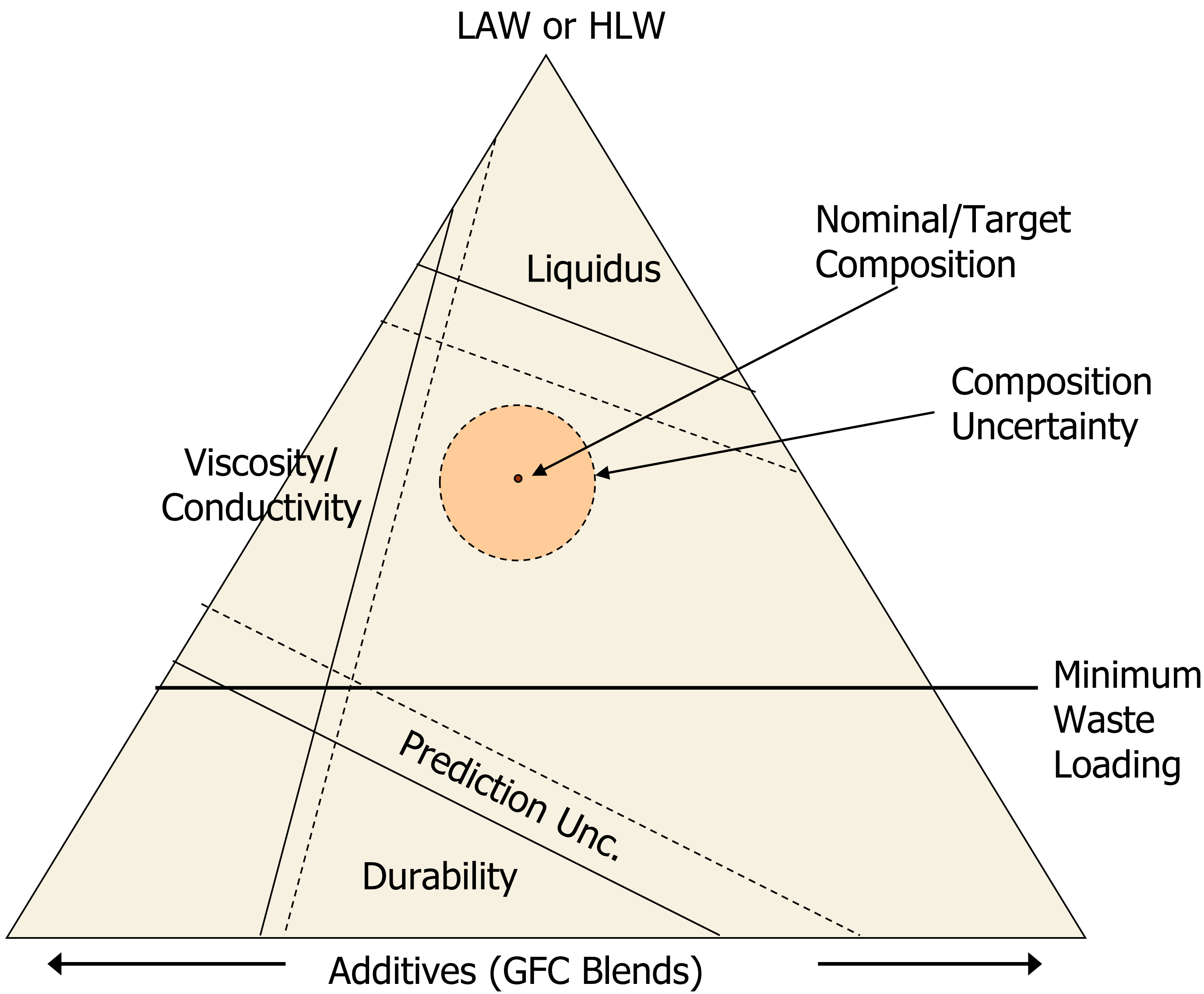
JD Vienna
GF Piepel
DS Kim
JV Crum
CE Lonergan
BA Stanfill
BJ Riley
SK Cooley
T Jin

U.S. DEPARTMENT OF ENERGY

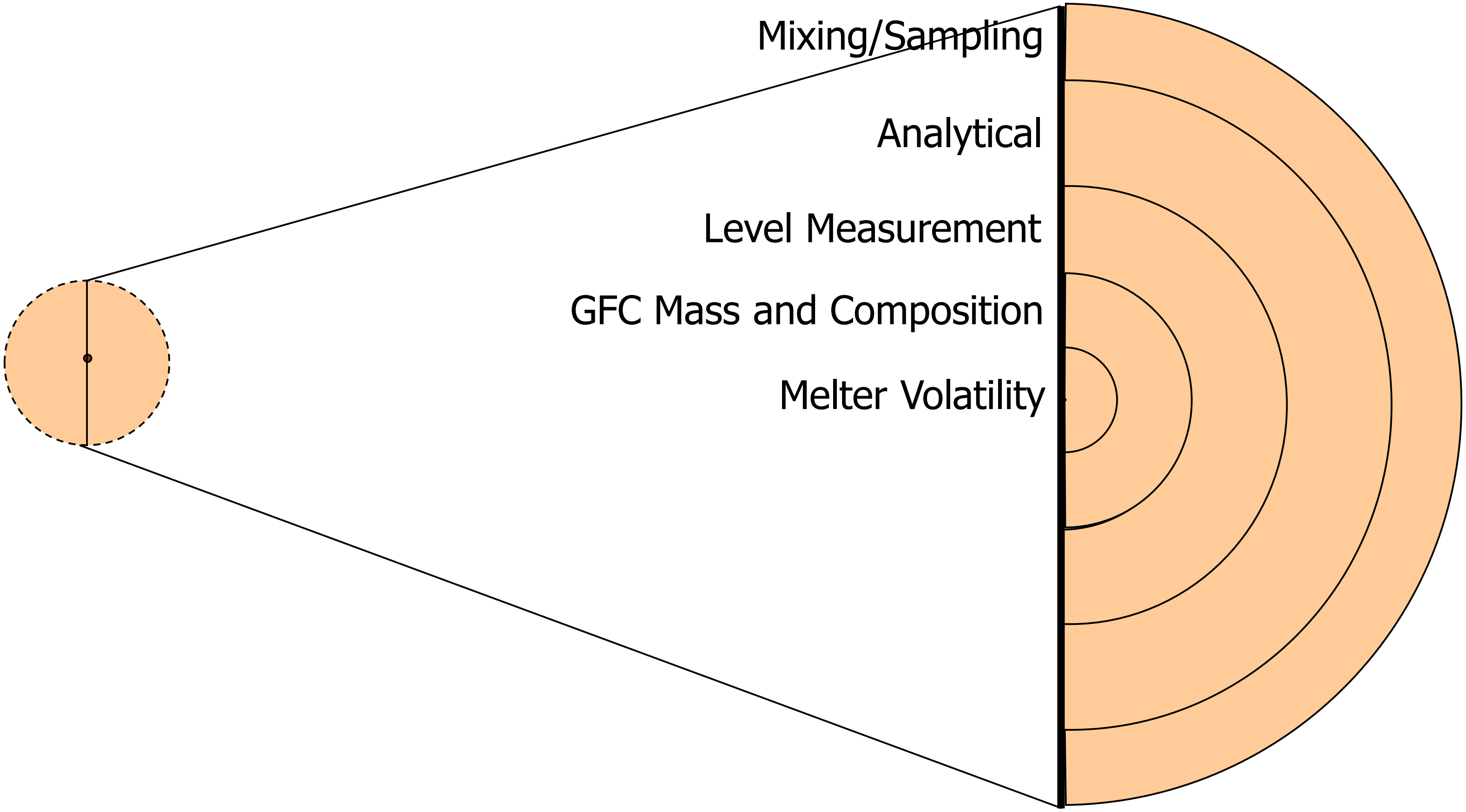
Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

Requirement	Value	Baseline Algorithm	Advanced Algorithm
Processability			
Melt Viscosity	$2 \le \eta_{1150°C} \le 8$ Pa·s $\eta_{1100°C} \le 15$ Pa·s	Property model	Property model
Melt Conductivity	$10 \le \varepsilon_{1100°C}$ S/m $\varepsilon_{1200°C} \le 70$ S/m	Property model	Property model
Salt Accumulation	No salt accumulation	Comp. interpolation	Property model
Melter Corrosion	K-3 neck corrosion ≤ 1 mm/6-day	Comp. interpolation	Property model
Crystallization	Crystal fraction at 950°C ≤ 1 vol%	Comp. interpolation	Property model
Minimum WL	$Na_2O \ge 14, 3, 10$ wt% for env. A, B, C	Mass balance	N/A
Cs-137 Limit	Cs-137 < 0.3 Ci/m^3	Mass balance	Mass balance
Product Quality			
PCT Response	$NL_B, NL_{Na}, NL_{Si} \le 2\ g/m^2$	Property model	Property model
VHT Response	$R_{200°C} \le 50\ g/m^2/d$	Property model	Property model
LDR Compliance	Extend HLVIT to UHC	Petition	Petition
Crystal Impacts	PCT & VHT predictably satisfy constraints	Comp. Interpolation	Property model
Class C Limits	Glass < Class C	Mass balance	Mass balance
Sr-90 Limit	Sr-90 < 20 Ci/m^3	Mass balance	Mass balance
Cs-137 Limit	Cs-137 < 3 Ci/m^3	Mass balance	Mass balance
Surface Dose Rate	Surface dose rate ≤ 500 mrem/h	Measure	Measure
Reporting			
Chemical Comp.	Report all constituents >0.5 wt%	Mass balance	Mass balance
Radionuclides	10 CFR 61.55 if > 1% table value Any > 7 Ci/m^3 in glass Any > 1% total activity Tc-99 if > 0.003 Ci/m^3	Mass balance	Mass balance

Schematic of Processing Window



Composition Uncertainty



Next Steps

Planned Work

Develop models and constraints with new data for plant operation (2019)

Update algorithm with the new models as they become available (2020)

Develop new graphical user interface (2019)

Verification & Validation (V&V) final algorithm software (2020)

Extend algorithm to support application of real-time on-line monitoring (2020)

Glass Formulation Options

Interpolation between successful glass compositions

- Successfully used for WTP baseline LAW glass formulation (validated)
- Reduce risk of process upsets
- Necessitates significant conservatism

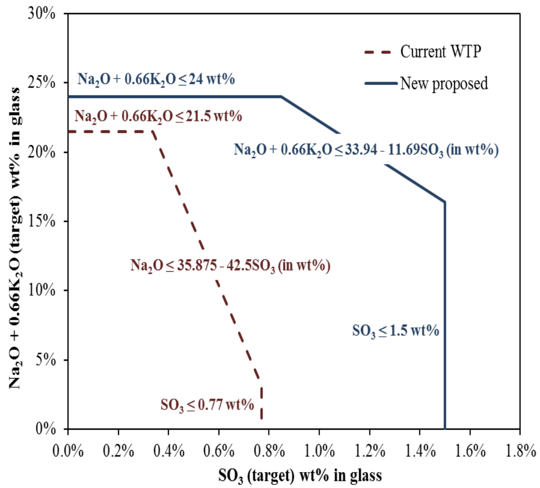
Numerical optimization using property models and constraints

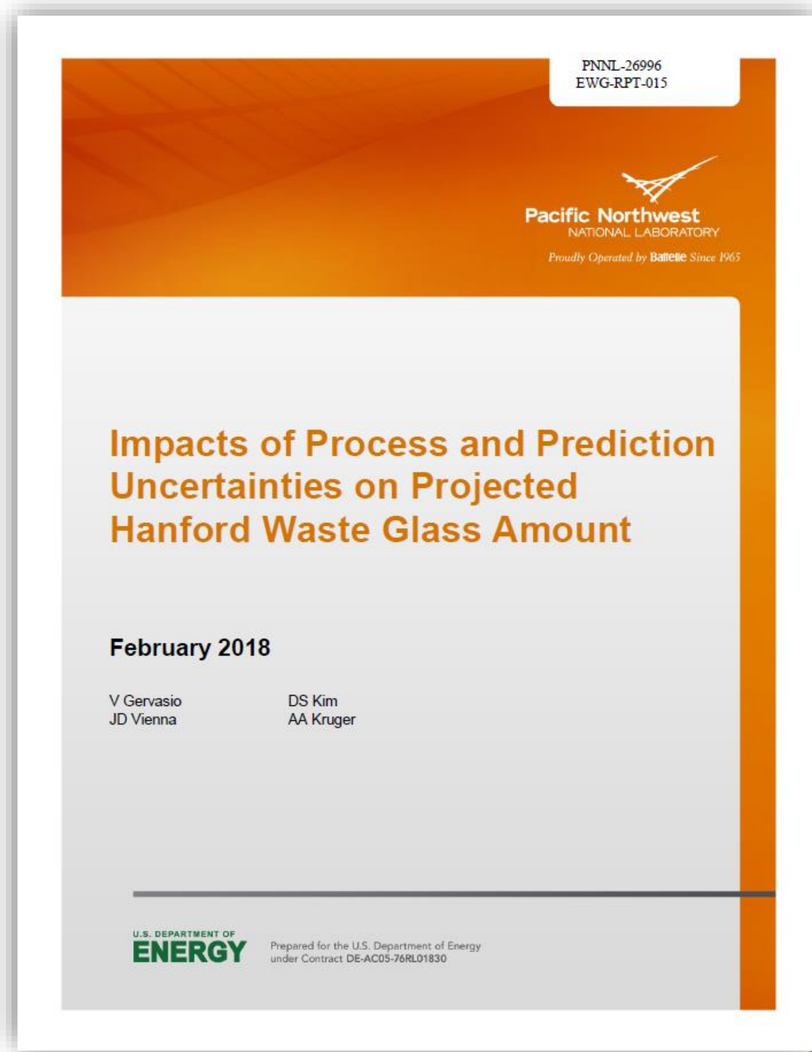
- Successfully used for WTP baseline HLW glass formulation (validated)
- Reduces conservatism
- Easily handles unanticipated waste feed compositions
- Directly addresses process uncertainties

Pegg, IL, IS Muller, KS Matlack, and I Joseph. 2018. "Process Control Approach to Implement High Waste Loading Glass Formulations for Hanford Low Activity Waste Vitrification," *Waste Management 2018*, Phoenix, AZ

Evaluation of Uncertainty Impacts Projected Glass

	No Unc	With Unc
Waste Loading Rules		
Mass (t) Containers RPD	282,350 51,243	282,562 51,282 (+0.1%)
No Waste Loading Rules		
Mass (t) Containers RPD	252,490 45,824 [-11%]	275,359 49,974 (+9%) [-3%]




PNNL-26996
EWG-RPT-015

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Impacts of Process and Prediction Uncertainties on Projected Hanford Waste Glass Amount

February 2018

V Gervasio DS Kim
JD Vienna AA Kruger

U.S. DEPARTMENT OF ENERGY

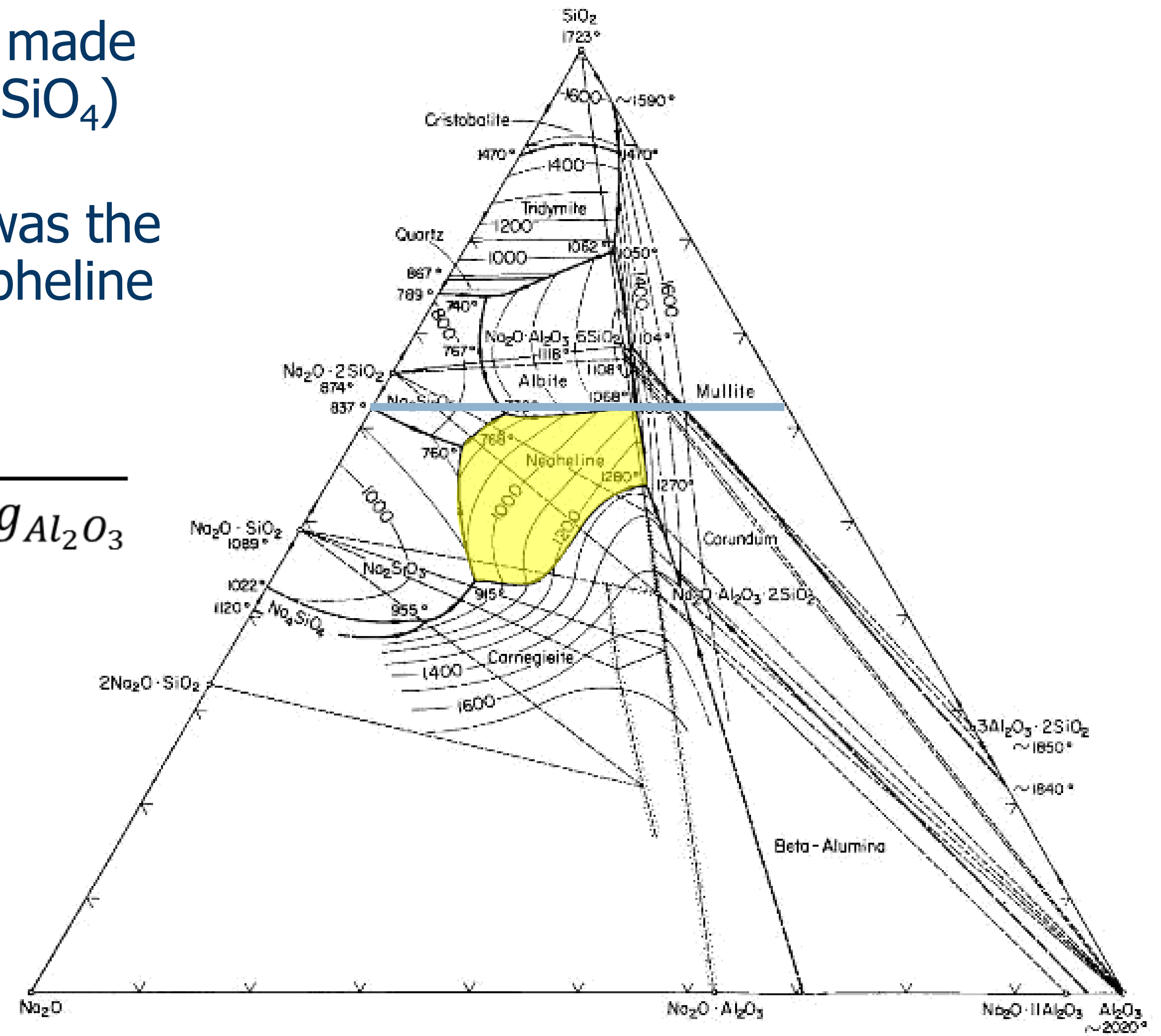
Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

High-Level Waste Vitrification

Nepheline Precipitation

- Many attempts have been made to predict Nepheline ($NaAlSiO_4$) formation
  - Most successful was the Li et al. 1997 Nepheline discriminator:

$$ND = \frac{g_{SiO_2}}{g_{SiO_2} + g_{Na_2O} + g_{Al_2O_3}}$$



Sulfur Tolerance in HLW Glass

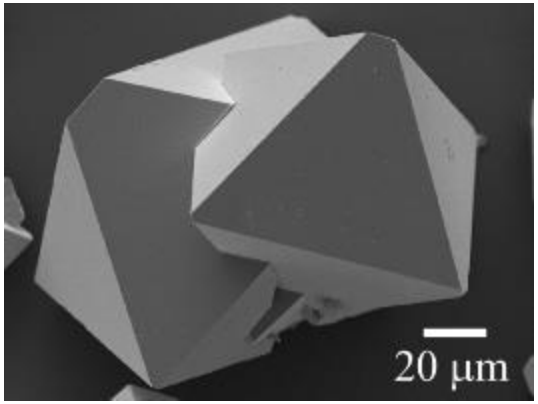
- At concentrations above the sulfur tolerance limit, a sulfate containing salt accumulates on the melt surface
- About 22% of the projected HLW feed batches to the WTP are expected to be limited by sulfate (WTP Contract Minimum 0.5%)

Crystal Tolerance

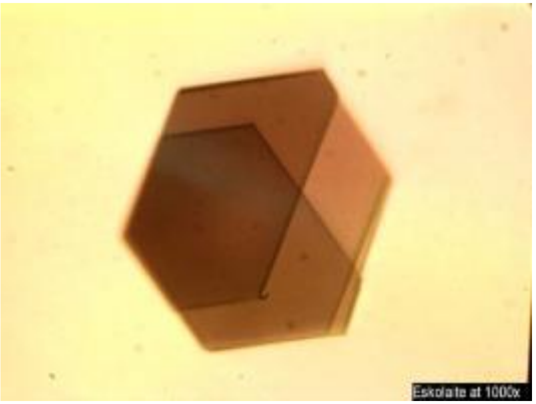
Two approaches considered:

- Matyas et al. 2013 model for predicting the accumulation rate of spinel in the pour-spout riser at 850°C
- Limit the crystal fraction in the melt

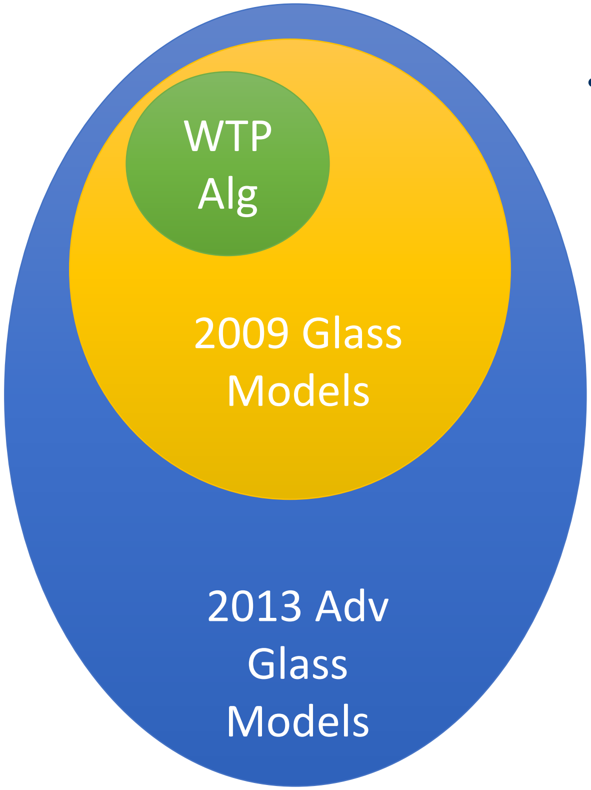
Spinel [Fe,Zn,Mn][Fe,Cr,Mn,Al]2O4



Eskolaite Cr2O3



Glass Work in a Nutshell



- Recent glass testing has covered significantly broader composition space and new methods have reduced conservatism
- Large increases in loadings of Al, Cr, Na, and S have been demonstrated at lab and melter scale

HLW Comp	WTP Baseline	HTWOS Models	Adv Models	Demon-strated
Al_2O_3	13	20	28	>30
Cr_2O_3	0.6	1.2	3	6
Na_2O	20	21.4	23	24
SO_3	0.44	0.6	1.6	1.9

Questions?


The Hanford Reach
White Bluffs Overlooking the Columbia River

Backup

Hanford History, cont.

2 Million m^3

Tank Waste Generated (1944-1988)

Started 1956
Reprocessed 190,000 m^3 (10%)

Started 1945
Disposed to Ground* 455,000 m^3 (23%)

Started 1956
Leaked to Ground 3800 m^3 (<1%)

Started 1951
Evaporated 1.1M m^3 (57%)

200,000 m^3 (10%)

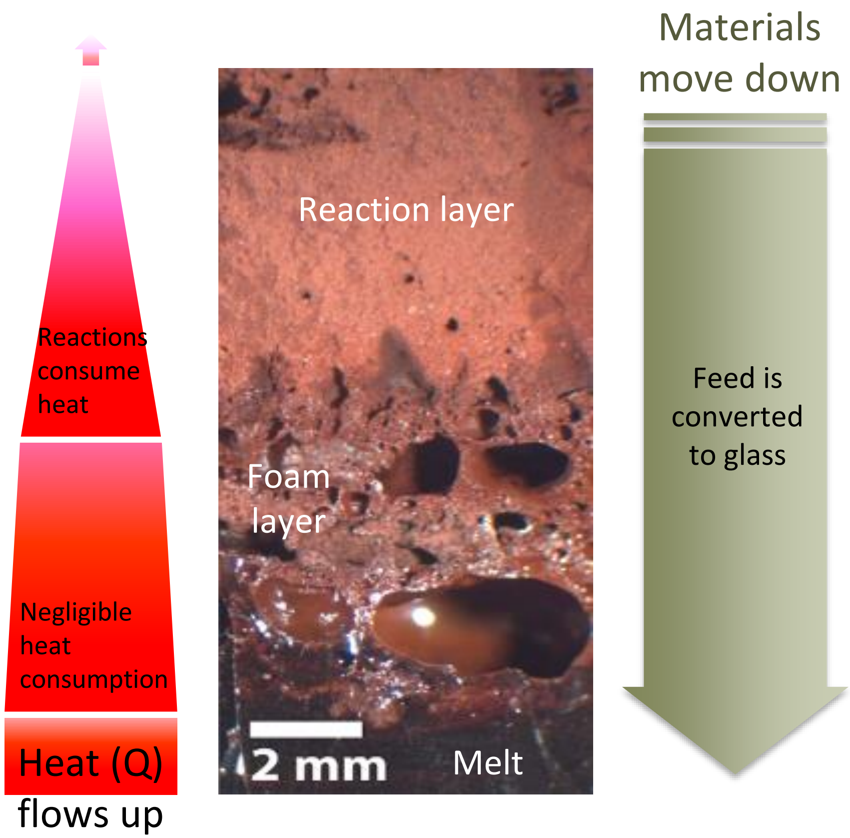
Formulating Glass

$$g_i = Ww_i + (1-W)a_i$$

$$P = \widehat{P}_T\,(g_1, g_2, \ldots, gn)$$

For a given waste composition (wi),
determine mineral addition (ai),
to obtain glass composition (gi),
with optimized properties (P),
and maximized waste loading (W)
The selection of properties to be optimized depends on melter technology and glass acceptability criteria

Heat Transfer



The feed-to-glass conversion heat is related to the rate of melting:

$$Q = (\Delta H + c_P \Delta T) j$$

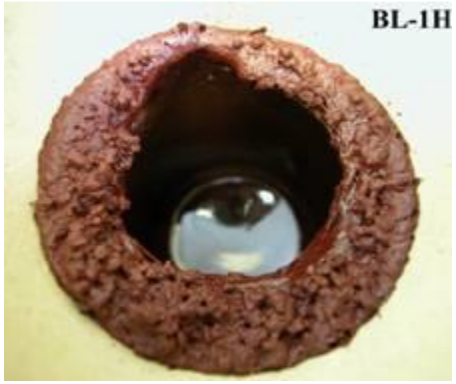
Q is delivered through the cold-cap bottom and transferred through the foam layer.

Q	conversion heat flux
ΔH	reaction heat
CP	heat capacity
ΔT	cold cap temperature difference
j	melting rate

Small-Scale Melt Rate

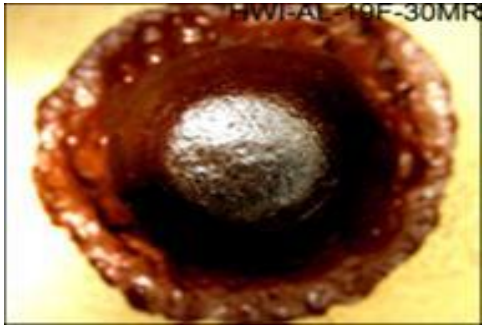
30 min

45 min

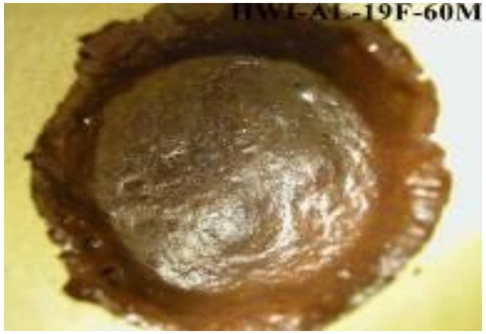


60 min

Initial Formulation



30 min



60 min

Improved Formulation

Improvements confirmed in one-third scale pilot melter tests

VSL-08R1360-1, Rev.0; VSL-10R1690-1, Rev. 0

EGA and O2 partial pressure by RAPIDOX

- The melt is highly oversaturated with oxygen. Such a high oversaturation is not likely to arise solely from the iron redox equilibrium, but also from the oxygen "stored" in the feed from earlier batch decomposition reactions (mostly nitrates).

Foaming Curve & Secondary Foam

- Detected CO2 in the foam layer as a residual gas from the feed reaction and involved in the primary foam.
- Detected O2 gas was from iron redox reaction and involved in the secondary foam.
- Influence of Gibbsite, Boehmite and Corundum

Foaming in High Bi-P HLW Glass Melts

- Results were used to modify glass formulations to mitigate melt foaming

Melt Rate & Loading in High Fe Glasses

- Improved formulations have been developed with both high melt rates and high waste loadings

Is the HLW requirement still based on repository requirements?

What is the current plan for a repository?

NWPA enacted in late 1982 after nearly 4 years of debate (P.L. 97-425)

NWPA Amendments of 1987

- Named Yucca Mountain as sole repository candidate site
- Established Nuclear Waste Technical Review Board to increase confidence in DOE program

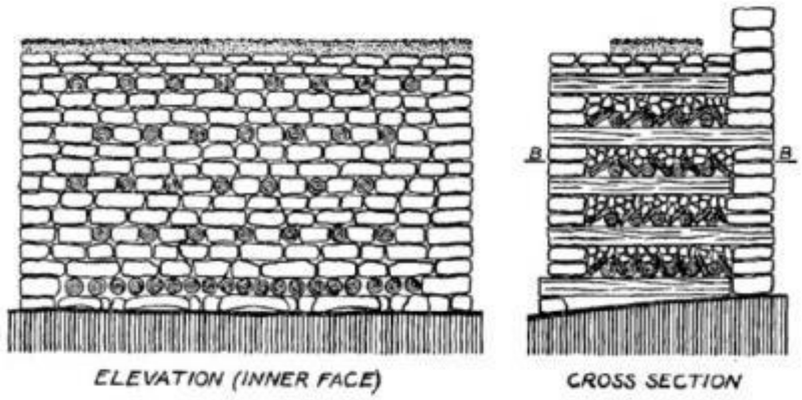
Energy Policy Act of 1992 (P.L. 102-486)

- Required EPA standards just for Yucca Mountain, based on NAS study

Civilian Radioactive Waste Management System
Waste Acceptance System Requirements Document, Revision 5

QUALITY ASSURANCE REQUIREMENTS AND DESCRIPTION, DOE/RW 0333P, Revision 20

Broborg Construction



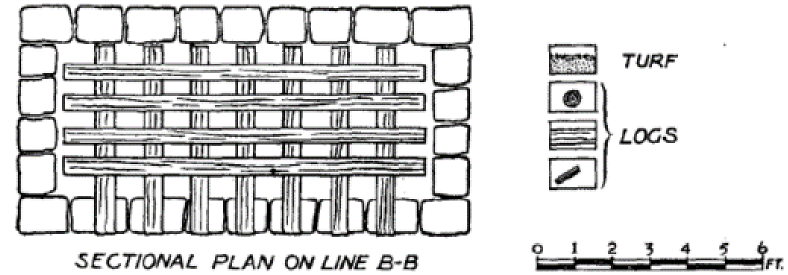
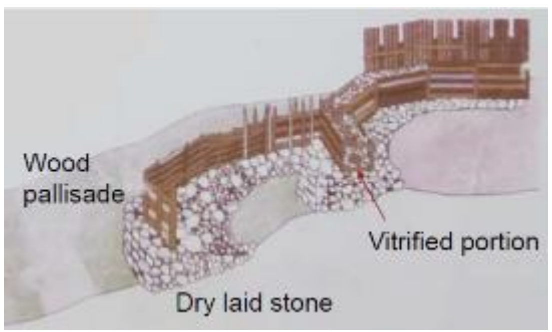
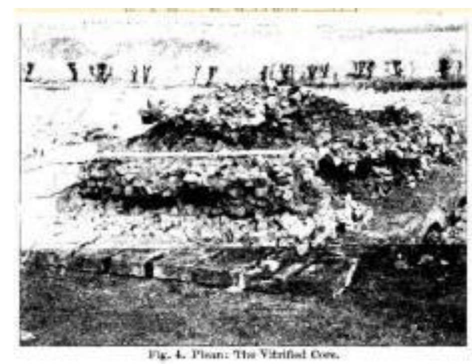


Fig. 1. Plean: The Model Wall.





- >10,000 Hillforts in Northern Europe (most from Iron Age 400-850 AD but some from 450 BC)
- Many are vitrified: Destructive? Incidental? Constructive?
- Iron beneficiation knowledge (burning charcoal/wood and controlling air flow) may have been used to achieve high vitrification temperatures at Broborg (800-1100°C)?

V.G. Childe and W. Thorneycroft, *Proceedings of the Society of Antiquaries of Scotland*, 72, 44-55 (1937)

Broborg Hillfort Project Team

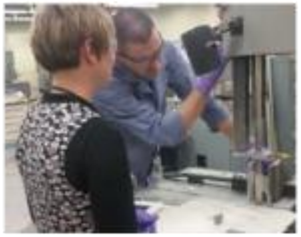
Our team is made up of Glass Scientists, Geologists, Materials Scientists, Archeologists, Geochemists, Art Conservation Scientists, Radiochemists, and Materials Analysis Specialists













- **Sweden:** Rolf Sjöblom (Tekedo AB), Eva Hjärthner-Holdar, Erik Ogenhall (Arkeologerna)
- **DOE:** Albert Kruger
- **PNNL:** David Peeler, Carolyn Pearce, Mike Schweiger, Tamas Varga, Bruce Arey, Micah Miller, Andy Plymale, Kayla Johnson, Danielle Saunders
- **NIST:** Jamie Weaver
- **WSU:** John McCloy, Mahmood Abusamha, Joseph Osborn, Jack Clarke (Sheffield University)
- **Smithsonian:** Ed Vicenzi, Robert Koestler, Paula DePriest, Tom Lam

Broborg Excavation Phase 2, Fall 2017

- Excavating down to original structure to obtain information on:
  - Broborg construction and history
  - Glass samples transecting wall to study thermal history, alteration and microbial impacts
  - Oriented glass samples for paleomagnetometry
  - Carbon dating charcoal and bone fragments from cooking fires

Summary and Conclusions

- Glassy areas have been identified in several Broborg samples
- Amorphous nature verified by µXRD
- Chemistry determined by µXRF and EDS
- Surface morphology and chemistry analyzed by SEM-EDS revealing presence of organics (bacteria, fungi, invertebrates)
- Microorganisms provide information on environmental conditions – water availability, pH etc.
- FIB sections extracted from glass analyzed by STEM-EDS to determine form and extent of glass alteration

Broborg glasses fulfill several important prerequisites for good analogues for nuclear waste glass: a similar chemical compositional space, similar mechanisms of corrosion, and alteration in similar, known environmental conditions

In what waste form will Tc be contained?

Can the Crystalline SilicoTitinate ion exchange resin from the Tank Side Cesium Removal system is incorporated into the HLW glass feed?

CST Feed

WTP baseline HLW composition-property models were developed for a glass compositional region with no Nb_2O_5 and < 1.2 wt% TiO_2, whereas > 3 wt% Nb_2O_5 and > 5 wt% TiO_2 can be expected in CST glasses.

The test results showed conversion of a CST feed to be moderately fast and that of a chabazite feed to be very fast, suggesting that processing these media is not likely to limit the glass production rates.

The results also show that the spent media can be vitrified either alone or in combination with WTP HLW streams with minimal impacts on waste loading or melt rates while producing fully compliant glass products.

Vitrification of Inorganic Ion-Exchange Media V Final Report, VSL-16R3710-1, Rev. 0

CST Feed

- All feed formulations with the ion exchange media were readily processed with ion exchange media waste loading up to 70 wt% and AY-102 HLW waste loading up to 31 wt% while meeting all WTP processing and product quality requirements and maintaining acceptable glass and feed processing properties.

- Glass production rates ranged from 800 kg/m^2/day for the HLW-IXC4-05 composition with AY-102 HLW oxides and CST.

- Gaseous emissions of nitrogen oxides and byproducts of incomplete combustion were nonexistent to minimal due to the lack of nitrates and organic carbon in the ion exchange media and the very low concentrations in the fully washed HLW waste.

Vitrification of Inorganic Ion Exchange Media Final Report, VSL-18R4380-1, Rev. 0

CST Feed Answers Wanted

Cesium Retention in the Product Glass during the Vitrification of Ion Exchange Media: Ideally, cesium captured on the ion exchange media would be incorporated into the glass upon vitrification. Conducting melter tests with ion exchange media containing cesium is required to determine the partitioning of cesium to the glass and melter exhaust during vitrification.

Incorporation into WTP Direct Feed HLW Pretreatment Strategy: The present testing was conducted with fully washed HLW solids. Incorporation of ion exchange media with unwashed or partially washed tank waste would provide additional opportunity for increasing total waste loading, waste processing rates, and reduction of pretreatment steps.

If the mission were to shift away from Pretreatment toward a direct feed HLW approach, how would that affect the total number and composition of the glass canisters?

Would there be any new problems to solve?

Background

- Sludge treatment in Pretreatment is primarily driven by desire to effectively leach and wash the HLW fraction of tank waste
  - Caustic leaching to remove primarily Al
  - Oxidative leaching to remove Cr
  - Washing to remove primarily Na, S, and leached Al and Cr
  - All driven to reduce the amount of glass produced to reduce mission length and cost of HLW glass management

- Several recent developments bring into question if sludge treatment in PT is the optimal River Protection Project flowsheet option
  - New glass development efforts have shown that significant improvements in Al, Cr, Na, and S loadings are likely, reducing the PT requirements
  - Flowsheet models currently project HLW melters idle for large fractions of the mission (balancing throughput between LAW and HLW is the goal)
  - Sludge treatment in PT is the single largest cause for technical issues and throughput challenges, negatively impacting plant startup schedule

Reduced Washing

- Preliminary studies have been completed by VSL to evaluate the impacts of under-washing on Direct Feed High-Level Waste (DFHLW) glass formulation
  - Two example tanks (selected as potential DFHLW feeds)
  - Feeds with 0, 1, 2, and complete washing were tested
  - Testing performed at DM100 scale
- Paper studies and crucible testing were performed to evaluate impact of washing efficiency on projected glass volumes using baseline (VSL) and advanced (PNNL) glass models
  - No significant advantage to washing for many waste tanks studied
  - A modest difference in can count for some wastes (e.g., AZ-101 and AZ-102) may drive the decision on washing

Risk could be significantly reduced by immobilizing over 50% of the curie content of the tanks in the first thousand canisters of HLW glass.

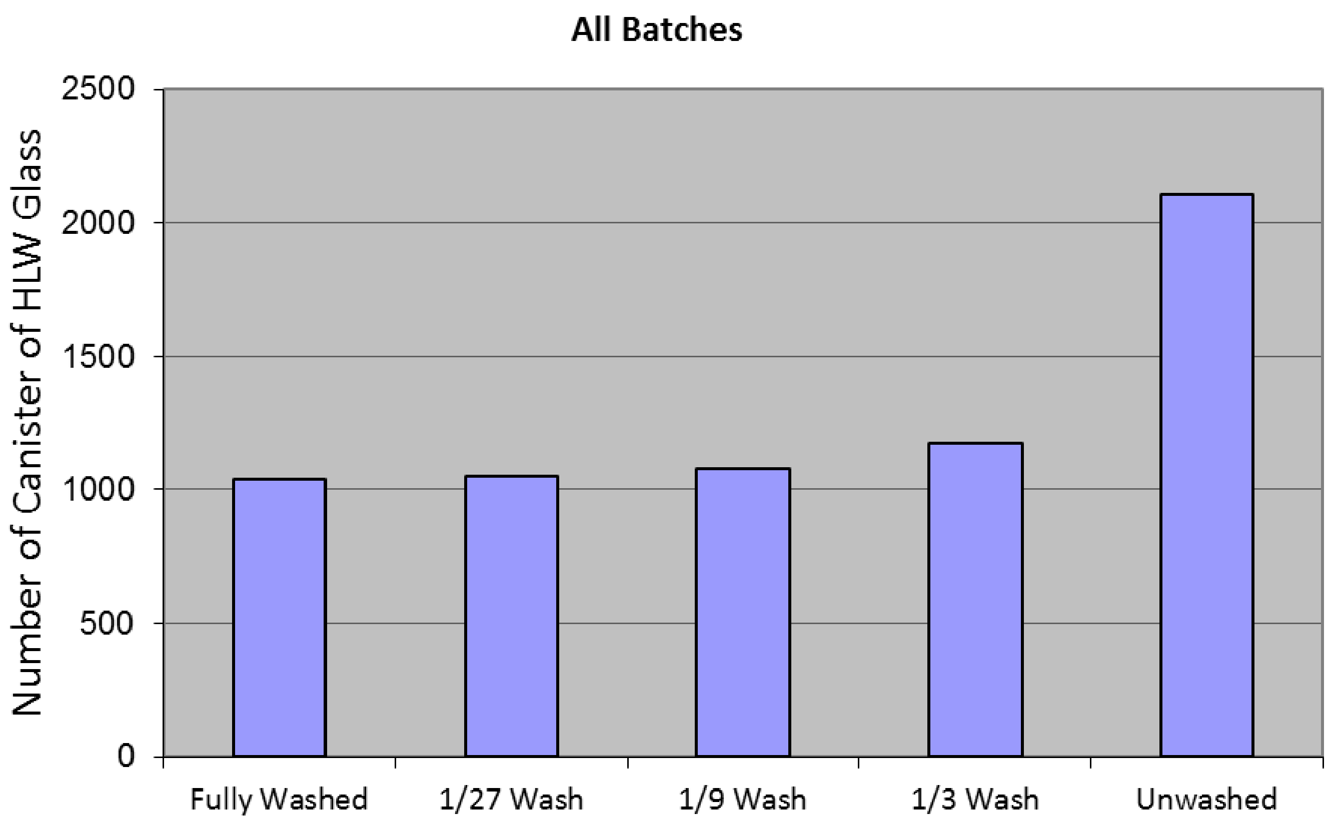
DFHLW 200East Area

241-A-103
241-A-104
241-A-105
241-AX-101
241-AX-102
241-AX-103
241-AX-104
241-AY-101
241-AZ-101
241-AZ-102
241-AP-102/241-AY-102

241-A Tanks Retrieved into 241-AP-106

241-AX Tanks Retrieved into 241-AZ-102

DFHLW Canister Projections



HLW glass produced in aggregate by Group 2 (16 Tanks) as a function of wash cycles. "1/3 Wash"=1 cycle; "1/9 Wash"=2 cycles, "1/27 Wash"=3 cycles.

- Other WTP DFHLW: The present and previous testing are based on two HLW tank compositions from the Hanford tanks. Subsequent work should extend these results to address the full range of HLW direct feeds expected to be processed at the WTP. In particular, HLW feeds for which the supernate is high in sulfate and/or halides need to be evaluated since the acceptable limits for these components in HLW glass are much lower than those for sodium. Also, identification of tanks requiring no or minimal pretreatment such as A-104, could expedite the processing of HLW at WTP.

- Salt Formation and Metal Corrosion: The potential for molten salt formation and increased metal corrosion (bubblers, thermowells, levels detectors, etc.) increases as the levels of halides and sulfates in the HLW feed increase. Consequently, for HLW feeds for which the supernate is high in sulfate and/or halides, these properties will determine the level of washing that is required to reduce these species to acceptable levels. Testing is needed to define these limits.

- Off Gas

- Settling of Pu Particles